Carbides and nitrides Ni-Mo phases supported on Mesoporous Al_2O_3 and MCM-41 materials from ammine salts precursors as new route of synthesis

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Introduction

The environmental pollution due to emission of toxic gases, generated by the increment it the fuels of petroleum every time but heavy and with a bigger concentration of impurities, it acts as poisons in the subsequent processes of refinement oil for the obtaining of light fractions, this has motivated the necessity to develop new catalysts that possess a bigger activity and better physical properties able to support severe operation conditions for the treatment of heavy oils fractions. Inside these new materials the transition metals nitrides and carbides like Mo and W are which had excellent physicochemical proprieties the current demands of the hydrodesulfurization processes. It has been find that the carbides and nitrides of a wide variety of chemical elements provide a great diversity of desirable properties as they are: catalytic activity or break of many chemical bonds, hardness, electric conductivity, among others. The Alumina (Al_2O_3) is the support material more broadly n used alone, for that, due it is cheap, besides being structurally stable, because it can be prepared with a wide variety of pore size and distributions of size of pores, but also to be a very active support as catalyst. Especially the γ alumina when they are desirable high surface areas, high temperature and mechanical stability. On the other hand, recently a new family of crystalline aluminum-silicates has been discovered by Mobil Oil Company with a hexagonal structure (MCM-41). These aluminum-silicates are very attractive due to their arrangement hexagonal uniform of pores, with an interior diameter of pore in the range of 20 at 100 A, composed for an it assembles supramolecular, depending on the synthesis conditions. Making them very attractive molecularly, but they have low catalytic properties for what is added a material that provides them this function. A very important factor in the hydrodesulfurization of heavy fractions is the distribution of the size pore which influences the activity of the catalyst[1].

Experimental

The alumina was prepared starting from of aluminum hydroxide (5 gr.) an precursor mixed with a suitable quantity of activated carbon (20, 15, 10% in weight of active carbon with a smaller particle size to 200 mesh) kneaded with a peptizing agent (1% nitric acid solutions), and extruded with a piston extruder producing extrudates of 1.6 mm. of diameter. The final extrudates were calcined at 923 ºK for 4 hours in a oxygen flow, temperature was necessary for the obtaining of the γ- Al_2O_3 phase and remove the pore forming materials from supports (active carbon).For the synthesis of the MCM 41, one prepares a mixture of deionized water and cetil-trimetil-ammonium bromide (CTAB), to which is added NH_4OH, is allowed to stirring the mixed solution, after the agitation is added tetraethyl-orto-silicate, stirring, filter, and dry to retire the humidity. Finally, the material was calcined at 813ºK for 6 hours in oxygen flow to eliminate the whole organic material. The metals were impregnated by means of the sprayed technique all precursor were dissolved means of a solution of NH_4OH-H_2O, this solution contains the salt of the metal to impregnate in the certain concentrations. The salts used for the impregnation were: nickel nitrate and ammonium heptamolybdate. After the impregnation, the materials dried off from 383ºK for finally to roast them up to 773ºK.

The transition metals oxides were placed in a reactor which will be placed inside the horizontal tubular furnace and by means of heating ramps, depending from the metal to prepare, they will decrease in an atmosphere of NH_3 until forming an oxinitride (˜823ºK). After this temperature it will be made pass a mixture from CH4/H2 to varied flows up to 973ºK and stayed the flow in the final temperature for 1 hour. The final carbide will be cooled until the room temperature, and passivated in a mixture of O2/Ar (1%O_2) to prevent the mass oxidation. For the synthesis of the nitrides a precursor is obtained for the Ni_2Mo_3N it was prepared by the breakup of $Ni(NO_3)•6H_2O$, $(NH_4)6Mo_7O_{24}•4H_2O$ and hexamethylenetetramine (HMT) whit a molar rate of 14:3:34 in a solution to 15% of $NH_3•H_2O$.same procedure on synthesis of carbides was used but the inert gas was changed by argon.

X-ray diffraction was performed by Diffractometer BRUKER model AXS D8000 ADVANCE by powders technique. Textural proprieties were performed by QUANTA CHROME, model AUTOSORB -1.

Results and discussions

X-ray diffractor patterns showed the typical peaks of MCM-41 and high dispersion of bimetallic phases. Mesoporous size of materials were founded by BET technique according whit figure 2.

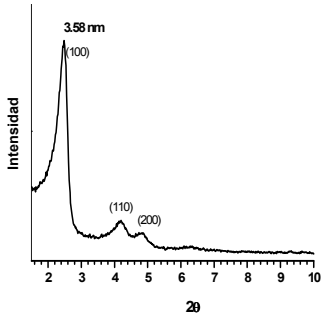

Figure 1. Pattern of diffraction of the support pure MCM-41

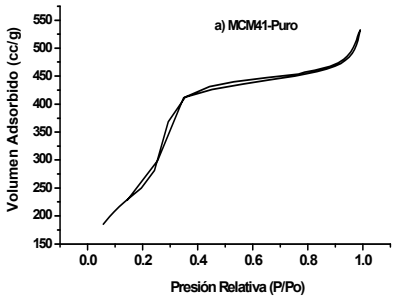

Figure 2 Isotherm of adsorption-desorption of the supports of MCM -41pure

References

1. Wang Huamin, Li Wei, Zhang Minghui, Chem. Mater, 17 (12), 3262-3267, (2005)